

12

**EUROPEAN PATENT APPLICATION**

21 Application number: 86116946.4

51 Int. Cl.<sup>4</sup>: C25B 11/20 , H01M 8/10

22 Date of filing: 05.12.86

30 Priority: 09.12.85 US 806713  
09.12.85 US 806715  
09.12.85 US 806717

43 Date of publication of application:  
01.07.87 Bulletin 87/27

64 Designated Contracting States:  
AT BE CH DE ES FR GB IT LI LU NL SE

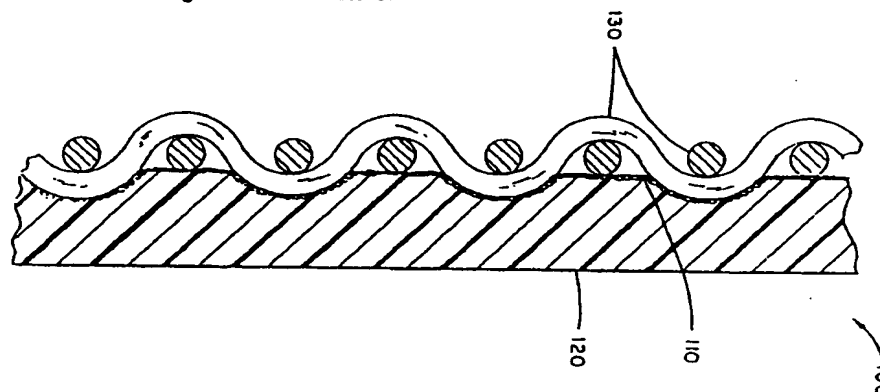
71 Applicant: **THE DOW CHEMICAL COMPANY**  
2030 Dow Center Abbott Road P.O. Box 1967  
Midland, MI 48640(US)

72 Inventor: McIntyre, John M.  
319 Petunia  
Lake Jackson Texas 77566(US)  
Inventor: Birdwell, Jeffrey D.  
207 Nasturtium  
Lake Jackson Texas 77566(US)  
Inventor: Smith, Bruce R.  
58 Blackgum Court  
Lake Jackson Texas 77566(US)

74 Representative: Huber, Bernhard, Dipl.-Chem.  
et al  
Patentanwälte H. Weickmann, Dr. K. Fincke  
F.A. Weickmann, B. Huber Dr. H. Liska, Dr. J.  
Prechtel Möhlstrasse 22 Postfach 860 820  
D-8000 München 86(DE)

54 An improved solid polymer electrolyte electrode.

57 The invention is a solid polymer electrolyte structure comprising a membrane sheet (120); a plurality of electrically conductive particles (110); and an electrically conductive, hydraulically permeable matrix structure - (130); wherein the electrically conductive particles and the electrically conductive matrix are in physical and electrical contact with each other and are embedded in or bonded to the membrane sheet. The invention also resides in a method of forming the SPE structure.



Xerox Copy Centre

**EP 0 226 911 A1**

## AN IMPROVED SOLID POLYMER ELECTROLYTE ELECTRODE

The present invention provides for a solid polymer electrolyte (SPE) structure that minimizes the electrical resistance between a current collector and an embedded or bonded electrode.

Solid polymer electrolyte (SPE) cells refer to cells in which one or both electrodes are bonded to or embedded in a polymeric ion exchange membrane. Such cells are rather well known in the art and are discussed in detail in the following U.S. Patent Nos. 4,315,805 to Darlington, et al. (February 16, 1982); 4,364,815 to Darlington, et al. (December 12, 1982); 4,272,353 to Lawrence, et al. (June 9, 1981); and 4,394,229, to Korach (July 19, 1983).

In SPE cells, a current collector is pressed against and contacts the electrode and provides a pathway for electrical current to flow from a power supply to the electrode. Current collectors are electrically conductive, hydraulically permeable matrices which may take a variety of shapes, sizes, and types, including metallic window screen, punched metallic plates, expanded metals, and the like. The following U.S. Patents describe some commonly-used types of current collectors: No. 4,299,476 to Korach - (November 10, 1981); No. 4,468,311 to de Nora, et al. (August 28, 1984); and No. 4,215,183 to MacLeod - (July 29, 1980).

SPE cells often have major problems due to the high electrical resistance between the embedded or bonded electrodes and the current collectors which are pressed against the electrode. Many workers in the art have attempted to solve the high resistance problem in a variety of ways. Some solutions include the use of a mattress as shown in U. S. Patent No. 4,468,311 issued to de Nora, et al. (August 28, 1984); or by applying the electro-catalyst directly to a conductive carbon cloth which acts as the current collector, as described in U.S. Patent No. 4,239,396 issued to Allen, et al. (October 6, 1981).

The invention particularly resides in a solid polymer electrolyte structure comprising:

- (a) a membrane sheet;
- (b) a plurality of electrically conductive particles; and
- (c) an electrically conductive, hydraulically permeable matrix structure; wherein the electrically conductive particles and the electrically conductive matrix are in physical and electrical contact with each other and are embedded in or bonded to the membrane sheet.

The single figure illustrates the SPE structure 100 of a present invention comprising a membrane sheet 120, a plurality of electrically conductive particles 110, and an electrically conductive, hydraulically permeable matrix 130.

As a result of the intimate contact between the membrane sheet, the electrically conductive particles, and the electrically conductive, hydraulically permeable matrix (which serves as a current collector and which is connected to a power supply), the resistance to the flow of electrical energy is minimized and, thus, the cell operates more efficiently than cells employing the SPE structures of the prior art.

The SPE structure of the present invention includes embodiments where electrically conductive particles are bonded to or embedded in one, or both, sides of the membrane sheet.

The SPE structure 100 is composed of a membrane sheet 120 which has a plurality of electrically conductive particles 110 embedded into it. The particles are in physical and electrical contact with an electrically conductive, hydraulically permeable matrix 130, which is also embedded into the membrane sheet 120.

The membrane sheet divides the anode compartment from the cathode compartment and limits the type and amount of fluids and/or ions that pass between the anode compartment and the cathode compartments. The membrane may be a single layer membrane or a multi-layer composite membrane.

The membrane may be constructed of a fluorocarbon-type material or of a hydrocarbon-type material. Such membrane materials are well known in the art. Preferably, however, fluorocarbon materials are generally employed because of their chemical stability.

Non-ionic (thermoplastic) forms of perfluorinated polymers described in the following U.S. Patents are suitable for use in the present invention: U.S. Patent Nos. 3,282,875; 3,909,378; 4,025,405; 4,065,366; 4,116,888; 4,123,336; 4,126,588; 4,151,052; 4,176,215; 4,178,218; 4,192,725; 4,209,635; 4,212,713; 4,251,333; 4,270,996; 4,329,435; 4,330,654; 4,337,137; 4,337,211; 4,340,680; 4,357,218; 4,358,412; 4,358,545; 4,417,969; 4,462,877; 4,470,889; and 4,478,695; and European Patent Application 0,027,009. Such polymers usually have an equivalent weight in the range of from 500 to 2000.

To allow the cloth and the electrically conductive particles to be embedded into the fluorocarbon membrane, it is desirable for the fluorocarbon membrane to be in its thermoplastic form. It is in a thermoplastic form when it is made and before it is converted into an ion exchange form. By thermoplastic form, it is meant, for instance, that the membrane has  $\text{SO}_2\text{X}$  pendant groups rather than ionically bonded

5  $\text{SO}_2\text{Na}$  or  $\text{SO}_2\text{H}$  pendant groups, where X is -F,  $-\text{CO}_2$ ,  $-\text{CH}_3$ , or a quaternary amine.

Particularly preferred fluorocarbon materials for use in forming membranes are copolymers of monomer I with monomer II (as defined below). Optionally, a third type of monomer may be copolymerized with I and II.

The first type of monomer is represented by the general formula:

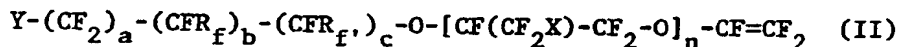
10  $\text{CF}_2=\text{CZZ}'$  (I)

where:

Z and Z' are independently selected from -H, -Cl, -F, and  $-\text{CF}_3$ .

The second monomer consists of one or more monomers selected from compounds represented by the general formula:

15



20 where:

Y is selected from  $-\text{SO}_2\text{Z}$ , -CN,  $-\text{COZ}$ , and  $\text{C}(\text{R}_1\text{f})(\text{R}_2\text{f})\text{OH}$ ;

Z is selected from -I, -Br, -Cl, -F, -OR, and  $\text{NR}_1\text{R}_2$ ;

R is a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

$\text{R}_1\text{f}$  and  $\text{R}_2\text{f}$  are independently selected from perfluoroalkyl radicals having from 1 to 10 carbon atoms;

25  $\text{R}_1$  and  $\text{R}_2$  are independently selected from H, a branched or linear alkyl radical having from 1 to 10 carbon atoms and an aryl radical;

a is 0-6;

b is 0-6;

c is 0 or 1;

30 provided  $a+b+c$  is not equal to 0;

X is selected from Cl, Br, F, and mixtures thereof when  $n>1$ ;

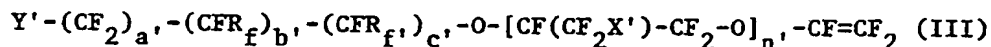
n is 0 to 6; and

$\text{R}_1$  and  $\text{R}_2$  are independently selected from F, Cl, Br, perfluoroalkyl radicals having from 1 to 10 carbon atoms and fluorochloroalkyl radicals having from 1 to 10 carbon atoms.

35 Particularly preferred is a monomer where Y is when  $-\text{SO}_2\text{F}$  or  $-\text{COOCH}_3$ ; n is 0 or 1;  $\text{R}_1$  and  $\text{R}_2$  are F; X is -Cl or -F; and  $a+b+c$  is 2 or 3.

The third and optional monomer suitable is one or more monomers selected from the compounds represented by the general formula:

40



45 where:

Y' is selected from F, Cl and Br;

$a'$  and  $b'$  are independently 0-3;

$c'$  is 0 or 1;

provided  $a'+b'+c'$  is not equal to 0;

50  $n'$  is 0-6;

$\text{R}_1$  and  $\text{R}_2$  are independently selected from Br, Cl, F, perfluoroalkyl radicals having from 1 to 10 carbon atoms, and chloroperfluoroalkyl radicals having from 1 to 10 carbon atoms; and

X' is selected from F, Cl, Br, and mixtures thereof when  $n>1$ .

55 Conversion of Y to ion exchange groups is well known in the art and consists of a reaction of Y with an alkaline solution.

While the fluorocarbon membrane is in its thermoplastic form, it is capable of softening when heated and hardening again when cooled. Thus, the cloth can be easily pressed into the membrane when the membrane has been heated. The temperature to which the membrane is preferably heated to make it sufficiently soft to allow the cloth to be embedded therein depends, to a great extent, on the chemical formulation of the membrane. In general, however, temperatures in the range of from 150°C to 350°C for membranes when  $Y = -SO_2F$  (as defined in Equation II above), or 150°C to 300°C for membranes when  $Y = -CO_2CH_3$  (as defined in Equation II above). Hydrocarbon-based membranes may (depending upon the exact composition of the hydrocarbon material) be heated to a temperature of from 100°C to 190°C.

For example, a membrane sheet may be prepared by hot pressing a sulfonyl fluoride powder having an equivalent weight of about 1000, as described in U.S. Patent No. 4,330,654 between two sheets of glass fiber reinforced polytetrafluoroethylene at a temperature of about 310°C under a pressure of about 0.75 tons per square inch (10,353 kPa) for about 1.25 minutes. The resulting sheet, having a diameter of from 15 to 18 cm, has a thickness of from 0.0025 to 0.4 mm, preferably, from 0.1 to 0.25 mm, most preferably, from 0.05 to 0.15 mm.

In the present invention, it is important to make an effective bond between the electrically conductive, hydraulically permeable matrix and the membrane. Such a bond may be made with or without the use of externally-applied pressure during bonding. It has been discovered, however, that better bonding is generally obtained when the membrane and the electrically conductive, hydraulically permeable matrix are first contacted and heated at zero pressure for about 1 minute, followed by application of a pressure of from 1 to 8 tons per square inch (13,780 to (110,240 kPa) for from 0.2 to 2 minutes.

The present invention requires that at least one of the electrodes be in the form of a plurality of electrically conductive particles embedded into the membrane sheet. This is what makes a SPE electrode. The electrode composed of a plurality of electrically conductive particles can be either the cathode or the anode. Optionally, both electrodes can be electrically conductive particles embedded into opposite sides of the membrane sheet. For the purposes of the present discussion, the forms of both electrodes will be described as though they are electrically conductive particles and will also be described as if they are separate, conventional electrodes.

Conventional anodes are usually hydraulically permeable, electrically conductive structures made in a variety of shapes and styles including, for example, a sheet of expanded metal, perforated plate, punched plate, unflattened diamond shaped expanded metal, or woven metallic wire. Metals suitable for use as anodes include tantalum, tungsten, columbium, zirconium, molybdenum, and preferably, titanium, and alloys containing major amounts of these metals.

Optionally, the anode may be an SPE electrode consisting of a plurality of electrically conductive particles embedded into the membrane sheet. Materials suitable for use as electrocatalytically active anode materials include, for example, activating substances such as oxides of platinum group metals like ruthenium, iridium, rhodium, platinum, palladium, either alone or in combination with an oxide of a film-forming metal. Other suitable activating oxides include cobalt oxide either alone or in combination with other metal oxides. Examples of such activating oxides are found in U.S. Patents Nos. 3,632,498; 4,142,005; 4,061,549; and 4,214,971.

Conventional cathodes are usually hydraulically permeable, electrically conductive structures made in a variety of shapes and styles including, for example, a sheet of expanded metal, perforated plate, punched plate, unflattened diamond shaped expanded metal, or woven metallic wire. Metals suitable for use as a cathode include, for example, copper, iron, nickel, lead, molybdenum, cobalt, and alloys containing a major proportion of these metals, such as low carbon stainless steel, and metals or alloys coated with substances such as silver, gold, platinum, ruthenium, palladium, and rhodium.

Optionally, as has been stated, the cathode may be an SPE electrode consisting of a plurality of electrically conductive particles embedded into the membrane sheet. Materials suitable for use as electrocatalytically active cathode materials include, for example, a platinum group metal or metal oxide, such as ruthenium or ruthenium oxide. U.S. Patent No. 4,465,580 describes such cathodes.

The electrically conductive particles, whether used as an anode or as a cathode are preferably finely divided and have a high surface area. For example, in the case of an oxygen or hydrogen electrode fuel cell, platinum black having a surface area of greater than 25 m<sup>2</sup>/g or high surface area (800-1800 m<sup>2</sup>/g) platinum on activated carbon powder (average particle size 10-30 microns) are quite suitable for use as the anode and the cathode. In the case of a chlorine cell, an electrode may be prepared in which ruthenium dioxide particles are prepared by thermal decomposition of ruthenium nitrate for 2 hours at a temperature of 450°C. The resulting oxide may then be ground using a mortar and pestle and the portion which passed through a 325 mesh sieve (less than 44 microns) used to prepare an electrode.

The electrically conductive, hydraulically permeable matrix which acts as a current collector to transmit electrical energy to or from the SPE electrode, may be composed of a variety of substances including carbon cloth, carbon paper, carbon felt, metallic screens, metallic felt, and porous metallic sheets. Preferably, however, the electrically conductive, hydraulically permeable matrix is a carbon cloth because  
 5 carbon cloth is readily available, performs well, is easily handled, and is relatively inexpensive.

The cloth most preferably used in this invention is one having a low electrical resistivity, is relatively inexpensive, possesses sufficient strength for fabrication, and has adequate surface properties, such as roughness, to provide good bonding between the ion exchange membrane and itself. It is also preferable to provide good electrical contact between the carbon cloth and the electrocatalytically active particles of the  
 10 electrode.

The type of carbon cloth suitable for use in the present invention is commercially available from a variety of sources including: Stackpole Fibers Co. sold under the names Panex PWB-3, PWB-6, KFB and SWB-8; from Union Carbide Corp. sold under the names WCA Graphite Cloth and VCK and VCA carbon cloth. Carbon cloth may also be woven from carbon fibers available from Fiberite Corp. sold under the  
 15 names Celion 1000, Celion 3000, Celion 6000, Celion 12000, or from Celanese Corporation sold as C-6, or G-50. These materials may vary in physical properties but are acceptable for use in the present invention as long as they are sufficiently strong to maintain their physical integrity during fabrication. Fiber size and weave patterns may also vary and are not critical to the successful operation of the present invention. Cloth useful in the present invention preferably has a thickness of from 0.05 to 0.65 mm and an electrical  
 20 resistivity of from 600,000 to 1375 microhm-centimeters. More preferably the cloth used in the present invention has a resistivity of approximately 1500 microhm-centimeters.

The SPE structure may then be fabricated by preparing the membrane in the thermoplastic form, embedding the electrocatalytically active particles into the membrane, bonding the current collector over the particles, and then converting the membrane to its ionic form by reacting it, in the case of  $-\text{SO}_3\text{F}$  pendant  
 25 groups, with NaOH under the following conditions: (1) immerse the film in about 25 weight percent sodium hydroxide for about 16 hours at a temperature of about  $90^\circ\text{C}$  (2) rinse the film twice in deionized water heated to a temperature of about  $90^\circ\text{C}$  using 30 to 60 minutes per rinse. The pendant group is then in the  $-\text{SO}_3\text{Na}^+$  form. Cations other than  $\text{Na}^+$  can be made to replace the  $\text{Na}^+$  if practical (such as  $\text{H}^+$ ).

The electrocatalytically active particles may be incorporated into the surface of the membrane using a  
 30 variety of techniques including, for example, pressing, slurring with a solvent and blending with the membrane or other polymer powders. Such techniques are rather well known in the art. One technique involves the use of platinum particles applied to carbon powder by being brushed evenly over a fluorocarbon membrane film in its thermoplastic form. The so-coated film is then placed between sheets of glass fiber reinforced polytetrafluoroethylene and hot pressed at a temperature of from  $240^\circ\text{C}$  to  $310^\circ\text{C}$  at a  
 35 pressure of from 0.5 to 1 ton/in<sup>2</sup> (6894 to 13,788 kPa) of pressure for from 1 to 10 minutes. The current collector may then be bonded to the so-coated membrane by placing it onto the membrane so that it is in contact with the particles, and hot pressing the combination at a temperature of from  $240^\circ\text{C}$  to  $310^\circ\text{C}$  at a pressure of from 0.5 to 1 ton/in<sup>2</sup> for a period of from 1 to 10 minutes.

The quantity of particles used on the membrane film to form the SPE electrode may vary depending  
 40 upon the activity of the electrocatalyst, its cost, etc. For chlor-alkali SPE membranes, the amount of catalyst used is usually from 0.4 to 1.0 milligrams catalyst/square centimeter of membrane area. There is an upper limit on the amount of particles which may be placed onto the membrane to prevent the particles from penetrating the membrane. The upper limit has been determined to be about 25 milligrams catalyst/square centimeter of membrane area.

An optional way of applying the electrically conductive particles is to make a suspension of the particles  
 45 in a liquid and spraying or pouring the suspension over the membrane, allow the liquid to evaporate, and then hot pressing the particles into the membrane with or without the carbon cloth in place. For example platinum and carbon particles may be slurried in dibromotetrafluoroethane and poured or sprayed onto a membrane. The dibromotetrafluoroethane is then allowed to evaporate. Carbon cloth current collectors can  
 50 then be hot pressed onto these so-formed electrodes.

A second alternative for preparing the SPE electrode of the present invention is to first prepare a thin film composed of electrocatalytically active particles bound together using a binder such as polytetrafluoroethylene or a membrane in its thermoplastic form. Preferably the binder material/catalyst combination is in the form of a porous film. This film can then be laminated between the current collector and  
 55 the membrane. For example, a film can be prepared from a blend of the thermoplastic form of an ion exchange membrane containing about 10 weight percent of 5 percent platinum on 30 micron carbon particles. This may be hot pressed at a temperature of  $310^\circ\text{C}$  at a pressure of 1 ton per square inch - (13,788 kPa) for 1.25 minutes to prepare a film having a thickness of less than 0.025 mm. This film can be

laminated between the carbon cloth current distributor and membrane by a conventional hot pressing technique. Thereafter, the carbon cloth may be embedded into the membrane sheet by preheating the membrane/carbon cloth pair at a temperature of 120°C at atmospheric pressure for about 30 seconds, followed by heating at the same temperature under a pressure of from 1 to 2 tons/in<sup>2</sup> for 225 seconds, then  
 5 heating under a pressure of from 2 to 3 tons/in<sup>2</sup> for about 60 seconds (for a hydrocarbon based membrane having a melting point of from 125°C to 140°C. Time interval temperature and pressure may vary depending on selection of type and thickness of membrane.

Optionally, the electrically conductive particles may be applied to the carbon cloth prior to the carbon cloth being embedded into the membrane sheet. Such a procedure involves preparing the cloth as  
 10 described in U.S. Patent No. 4,293,396, (October 6, 1981). The so-prepared cloth can then be bonded to the membrane by contacting and preheating the membrane/cloth pair at a temperature of about 240°C at atmospheric pressure for 60 seconds, then applying a pressure of from 4 to 6 tons/in<sup>2</sup> at a temperature of about 240°C for a period of from 40 to 120 seconds, followed by cooling to a temperature of from 20° to 25°C in air.

15 The solid polymer electrolyte structure of the present invention is useful in a wide variety of electrochemical cells including, for example, fuel cells for the continuous production of electrical energy; electrolysis cells for the production of chemical products; and batteries for the intermittent production of electrical energy.

20

### Claims

1. A solid polymer electrolyte structure comprising:

(a) a membrane sheet;

25 (b) a plurality of catalytically active and electrically conductive particles; and

(c) an electrically conductive, hydraulically permeable matrix structure;

wherein the particles and the matrix are in physical and electrical contact with each other and are embedded in or bonded to the membrane sheet.

30 2. The electrolyte structure of Claim 1 wherein the membrane sheet is selected from a hydrocarbon polymer and a fluorocarbon polymer.

3. The electrolyte structure of Claim 2 wherein the membrane sheet has a thickness of from 0.0025 to 0.4 mm and an equivalent weight of from 500 to 2000.

4. The electrolyte structure of Claim 1, 2 or 3 wherein the plurality of electrically conductive particles constitute an anode and are selected from oxides of ruthenium, iridium, rhodium, platinum, palladium and  
 35 oxides of a film-forming metal.

5. The electrolyte structure of Claim 1, 2 or 3 wherein the plurality of electrically conductive particles constitute a cathode and are selected from platinum group metals or metal oxides.

6. The electrolyte structure of Claim 5 wherein the plurality of electrically conductive particles are ruthenium or ruthenium oxide.

40 7. The electrolyte structure of Claim 1, 2 or 3 wherein said electrically conductive particles form an anode on one side of the membrane sheet and a cathode on the opposite side of the membrane.

8. The electrolyte structure of Claim 1, 2 or 3 wherein said electrically conductive particles form an electrode on one side of the membrane sheet and a porous metal plate forming an electrode on the other side of said membrane sheet.

45 9. The electrolyte structure of any one of the preceding claim wherein said hydraulically permeable matrix is selected from carbon cloth, carbon paper, carbon felt, metallic screens, metallic felt, and porous metallic sheets, said matrix having a thickness of from 0.05 to 0.65 mm and a resistivity of from 600,000 to 1375 microhm-centi meters.

50 10. The electrolyte structure of Claim 9 wherein the hydraulically permeable matrix is formed from carbon cloth or woven carbon fibers.

11. A method for forming a solid polymer electrolyte structure comprising:

(a) forming a mixture of a binder and a plurality of catalytically active, electrically conductive particles;

(b) forming the mixture into a particle containing film;

55 (c) contacting the film with a fluorocarbon membrane in its thermoplastic form;

(d) contacting the particle-containing film with an electrically conductive, hydraulically permeable matrix, thereby forming a laminate having a membrane on one side, a matrix on another side and a plurality of catalytically active particles therebetween; and

(e) applying sufficient pressure to the laminate to embed at least a portion of the matrix into the membrane while the membrane is in its thermoplastic form.

12. The method of Claim 11 wherein the binder is polytetrafluoroethylene or a fluorocarbon ion exchange active polymer in its thermoplastic form.

5 13. A method for forming a solid polymer electrolyte structure comprising:

(a) heating a fluorocarbon membrane, while it is in its thermoplastic form, to a temperature at which it softens;

10 (b) contacting a plurality of electrically conductive, catalytically active particles with at least a portion of one face of the membrane, while said membrane is in a softened state to form a membrane/particle composite;

(c) subjecting the membrane/particle composite to a pressure sufficient to embed at least a portion of the particles into the membrane;

(d) contacting the membrane/particle composite with an electrically conductive, hydraulically permeable matrix to form a particulated membrane/matrix composite, and

15 (e) subjecting the particulated membrane/matrix combination to a pressure sufficient to embed at least a portion of the matrix into the particulated membrane.

20

25

30

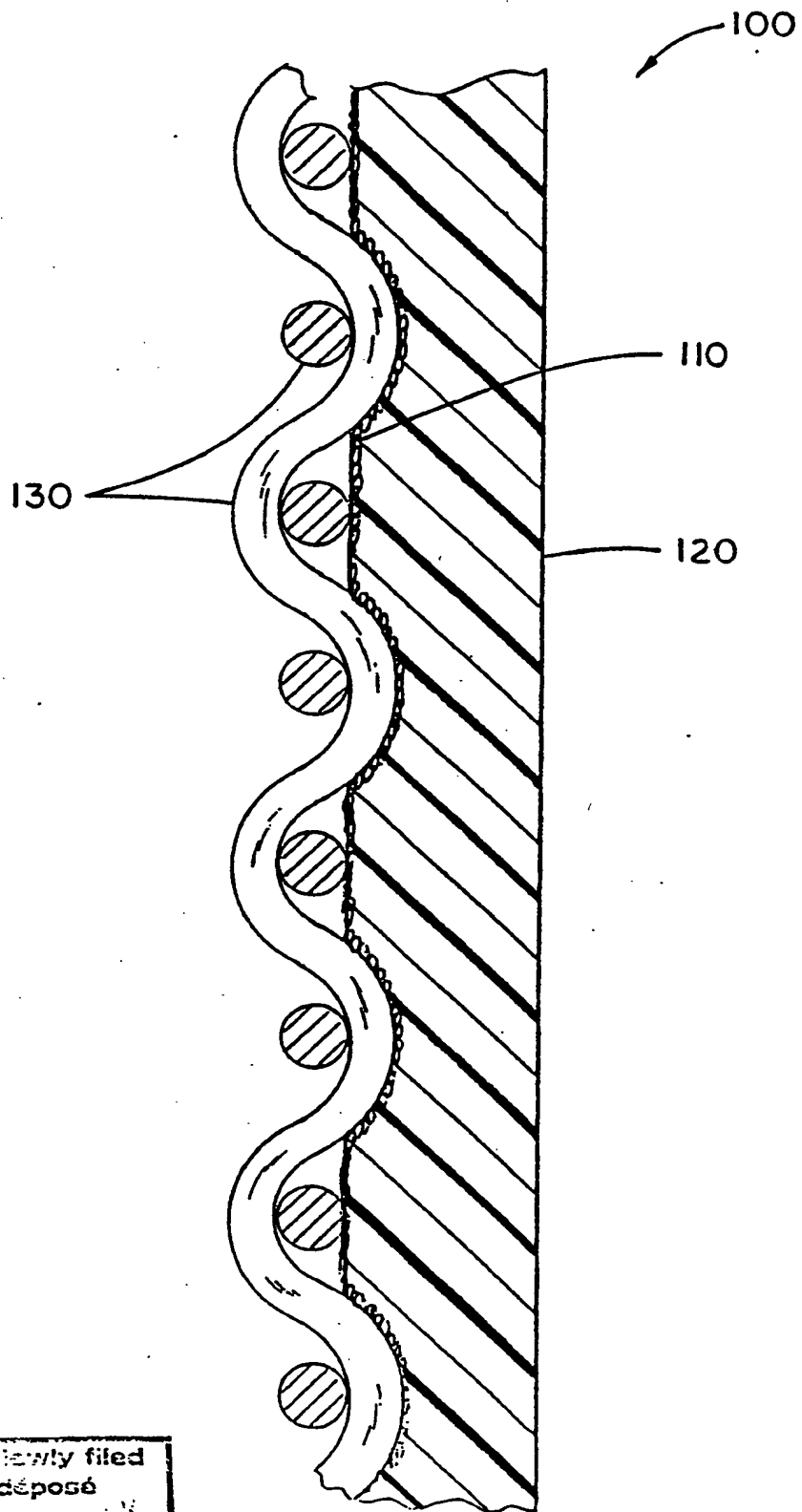
35

40

45

50

55



Neu eingereicht / Newly filed  
Nouvellement déposé





EP 86 11 6946

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 031 660 (PERMELEC ELECTRODE LTD) * Page 11, lines 1-5; page 12, lines 6-16; pages 20,21, example 6 *	1,2,4, 7,9	C 25 B 11/20 H 01 M 8/10
X	--- EP-A-0 081 251 (ELTECH SYSTEMS CORP.) * Page 13, lines 3-13; page 22, lines 1-25; pages 2,3 *	1-7	
Y		11-13	
Y	--- GB-A-2 117 797 (GENERAL ELECTRIC CO.) * Claims 1-3 *	11-13	
X	--- US-A-3 134 697 (L.W. NIEDRACH) * Column 5, lines 3-38 *	1,2,4, 5,7,9	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 25 B 9 H 01 M 8
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-03-1987	Examiner GROSEILLER PH.A.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	